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The Viscosities of Liquids and Their Vapor Pressures

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ALTHOUGH in recent years increasing attention has been given to the examination of the molecular state of liquids with a view to explaining their viscous behavior under varying conditions of temperature and pressure, few of the theories have as a logical consequence shed much light on the relationships between the viscosity and other properties of a liquid of which one of the most immediate is the vapor pressure.

The object of this paper is to discuss briefly the interrelationship of liquid viscosity and vapor pressure. It is, of course, well known that, in general, viscous liquids are found to have low vapor pressures and mobile liquids high vapor pressures, but the recent successful development[1] of a viscosity-temperature relation of the significant form

$$\log (1/\eta) = -A/T + B \qquad (1)$$

opens up immediately the whole question of the interconnection of the viscous and evaporation processes occurring in a liquid.

Before the recognition of the equation of the type of (1) it was apparent from the structure of the vapor pressure temperature formula of Bertrand and the viscosity temperature of Graetz that there was a deep seated connection between the two.

Porter as early as 1912[2] drew attention to the matter when he pointed out that the Ramsay-Young rule for the vapor pressures of two substances held in a similar manner for their viscosities. This he summarized by saying that if the vapor temperature relationship is expressed by $F(p) = a + b/T$ then the viscosity temperature relationship should be expressed by $F(\eta) = A + B/T$.

On this point attention should be drawn to the generalization of Wheeler[3] which covers the two cases mentioned above together with many others. Wheeler gives as the extended form of the Ramsay-Young rule:

> The reciprocals of the absolute temperatures, for which two given powers of a variable or pairs of variables which satisfy equations of the form, log (variable) $= a + b/T$, are in constant ratio, satisfy a linear equation.

It is significant that liquid polarizations follow this rule.

It appears advantageous before dealing with the direct relationship between viscosity and vapor pressure to examine the constants of the formulas

$$\log (1/\eta) = A - B/T. \quad (1a) \qquad \log p = A' - B'/T. \quad (2)$$

Eq. (2) has been shown to hold over restricted ranges with considerable accuracy[4] and may be more pertinently discussed than the extended Rankine formula. B', it must be remembered, is proportional to the latent heat of vaporization.

In formula (1a), however, B is a similar energy

[1] Andrade, Nature, March 1, 1930.

[2] Porter, Phil. Mag. [6] **23**, 458 (1912).

[3] Wheeler, Phil. Mag. **2**, 441 (1931).

[4] Herz, Zeits. f. anorg. Chemie **191** 62–64 (1930).

function and according to Dunn[5] may be associated with the quantity of energy that it is necessary to impart to a molecule to overcome the attraction of its neighbors. This we may call for short the heat of cohesion. Drucker[6] went further and pointed out that this energy should include both that involved in de-aggregation and that needed for the spatial orientation of the molecules. The latter was demonstrated to be small so that except in a few cases Drucker was able to show that B approximated to the latent heat of fusion. In view of this approximation perhaps the conception by Andrade in his derivation of formula (1a) of the liquid "crystallizing" temporarily in patches is particularly happy. Other derivations of a like formula depend on less reasonable assumptions and include doubtful steps.[7]

The physical significance of Eq. (1) has also been discussed by M. P. Iyer[8] and others.

Going one step further an equation of the type of (1) has been found to hold well for colloids. In this case however the energy function B has been considered representative of the heat of solvation of the particles.[9, 10] The recent work on the cybotactic condition of colloidal suspensions on parallel lines to that carried out for liquids appears however to provide a sounder explanation for the applicability of Eq. (1) than does the earlier solvation hypothesis.

Little attention has been paid to the actual application of the formula to experimental results. By taking the measurements of Taft and Malm[11] for a 3.8 percent solution of gum arabic and those of Bogue[12] for gelatin a plot of $\log(1/\eta)$ against $1/T$ yields in both cases a straight line.

Having now briefly dealt with the separate equations relating to viscosity and vapor pressure, let us consider the equations governing the relationship between the two.

Viscosity and vapor pressure have been found to be accurately connected by the empirical equation

$$\log(1/\eta) = \rho + \mu \log p. \tag{3}$$

In Drucker's paper[6] will be found a list of tabulated values of μ and ρ.

This equation may best be written

$$p^{\mu} \cdot \eta = c \tag{4}$$

and there is some evidence to show that for an ideal liquid this reduces to a fourth power law, $p \cdot \eta^4 = \text{const.}$ or in other words that the latent heat of vaporization is four times the latent heat of cohesion. Departures from this rule occur more especially for the strongly associated substances and fluids like mercury. Mercury and metallic liquids are frequently irregular in their behavior. For example, the successful work of Edser[13] on molecular attraction and the physical properties of fluids particularly in regard to the latent heat of vaporization failed for metallic liquids.

Let us now examine some of the consequences of the relation $\log(1/\eta) = \rho + \mu \log p$.

If we put $\rho = \log \beta$ we may write

$$p^{\mu} \cdot \eta = 1/\beta. \tag{5}$$

Some time ago Batschinski[14] showed that for saturated vapors of ordinary liquids the formula $p^{1/4} = At + B$ holds very well over the pressure range of approximately 2 atmospheres up to the critical pressure. Assuming the validity of this law and substituting in (5), we have

$$\{1/(\beta^{1/\mu} \cdot \eta^{1/\mu})\}^{1/4} = At + B,$$

$$\eta = (1/\beta)/(At+B)^{4\mu} = (1/\beta \cdot A^{4\mu})/(t+B/A)^{4\mu},$$

which is identical in form with the well-known Slotte formula. Unfortunately the numerical index does not correspond well with the Slotte index.

It of course follows from (3) that if the formula for p is given for the restricted ranges by $\log p = A' - B'/T$, then $\log(1/\eta) = C - D/T$ holds equally well for these ranges. In a similar manner if the variation of p with T is given more accurately by

$$\log p = A - B/T + C \log T,$$

then the variation of η with T follows the law

$$\log(1/\eta) = \gamma - \delta/T + \epsilon \log T.$$

[5] Dunn, Trans. Faraday Soc. **22**, 401 (1926).
[6] Drucker, Zeits. f. physik. Chemie **92**, 287 (1918).
[7] Lederer, Koll. Beiheft. **34**, 270–338 (1931).
[8] M. P. Iyer, Ind. J. Phys. **5**, 371–383 (1930).
[9] Sheppard, J. Rheology **1**, 471–483 (1930).
[10] Mark, Kolloid Zeits., Oct. (1930).
[11] Taft and Malm, J. Phys. Chem. **35**, 874 (1931).
[12] Bogue, J. Am. Chem. Soc. **43**, 1764 (1921).
[13] Edser, Brit. Ass'n Report on Coll. Chem. **4**, 57 (1922).
[14] Batschinski, Nature, p. 198, Feb. 5, 1927.

The question of the greater accuracy of the three-constant equation, $\log (1/\eta) = \gamma - \delta/T + \epsilon \log T$, has been raised a number of times but whether or no the claims in this direction can be substantiated needs careful consideration. Dunn gives evidence in support of the greater accuracy of this equation for octane, and Friend[15] in his recent book also indicates his support of the equation although despite his reference there, no figures appear to have been actually published by him.

In the formula (3) given above it has been pointed out that the constant μ represents the ratio between the latent heat of vaporization and the heat of cohesion.

Suppose we assume with Perrin[16] that the internal latent heat of vaporization may be associated with a characteristic frequency ν, i.e., $L_i = Nh\nu$. We have also $L = L_i + RT$.

It is not unreasonable to suppose that the heat of cohesion B may be associated with the same characteristic frequency ν.

Then as has been shown, $L = B/\mu$ or $L_i + RT = B/\mu$ or $Nh\nu + RT = Nh\nu/\mu$. Hence

$$Nh\nu(1/\mu - 1) = RT. \qquad (6)$$

Putting in the usual values of N, h and R, assuming that $T = T_{bpt}$ and taking the value of μ from the experimental curve for the substance in question, we find that the value of ν that is deduced is very near to that arrived at from the Lindemann formula

$$\nu = 2.80 \times 10^{12} (T_m/a \cdot V^{2/3})^{1/2}.$$

For example, for bromine which has the normal value of $\mu = 0.236$

Eq. (6) gives $\nu = 2.17 \times 10^{12}$;

Lindemann's formula gives $\nu = 1.75 \times 10^{12}$.

For mercury which has the very different and more unusual value for μ of 0.042

Eq. (6) gives $\nu = 0.58 \times 10^{12}$;

Lindemann's formula gives $\nu = 1.23 \times 10^{12}$.

The two values are seen to be in reasonable agreement.

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[15] Friend, *Textbook of Physical Chemistry*, p. 247 (1932), Griffin.

[16] Perrin, Ann. de Physique [9] **2**, 5–108 (1919).

Further Studies on the Relation Between Constitution and Association: Especially in Reference to Aromatic Compounds

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(Received June 19, 1932)

The fluidities of fifteen ortho, meta and para compounds have been measured at temperatures of 0°C to 100°C, except when the melting point of the compounds interfered with measurements at the lower temperatures. The specific volumes of 14 of these compounds have been measured at the same temperatures. From the atomic temperature constants of C, H, O, Cl, Br and N given by Bingham and Spooner, the associations of the compounds have been calculated, whenever possible, at fluidities of 50, 100 and 200 rhes. From these same constants, and that of F determined by the authors, the associations of 14 ortho, meta and para compounds run by Swarts have been calculated at equal fluidities. On the basis of the theory of protection, the associations of these 29 compounds and of 17 ortho, meta and para compounds studied previously have been correlated.

In the case of compounds containing two non-associating groups, (A) The fluidity-temperature curves of the meta and para compounds cross, the para compound having the higher temperature coefficient of fluidity. (B) At low temperatures, the ortho compound is the most associated, the para next, and the meta compound has the least association. (C) At high temperatures, the ortho compound is the most associated, the meta next, and the para has the least association.

In the case of aromatic compounds, containing one non-associating and one associating group, the differences will be less clearly marked, but: (A) In general, the ortho compound is the least associated, the meta next, and the para compound is most associated. (B) In the phenetidines, at low temperatures, the meta compound is more associated than the para compound, but, having a higher temperature coefficient of fluidity, its fluidity-temperature curve shows a tendency to cross that of para-phenetidine, and at high temperatures, the associations will run $o<m<p$. (C) Where the associating group is NO_2, the associations of the three isomers are nearly equal, with that of the meta compound being slightly lower than the associations of the ortho and para compounds.

In the case of compounds containing two associating groups, according to the theory, the associations should run $o<m<p$. Time was not available to run any of these compounds, and there are no fluidity data on them in the literature since all are solids at ordinary temperatures. In general, however, the boiling points of these substances, which vary in the same order as the association, run $o<m<p$ (Table V). Unfortunately, even these data are scanty.

It is shown that the theory of protection offers an explanation for the behavior noted above.

INTRODUCTION

FOR some time, efforts have been made to determine the effect on the association, of introducing any given chemical group into a compound.

Bingham and Fornwalt[1] have shown that in the case of the esters the addition of non-associating groups, such as CH_2, decreases the association, as the associating carboxyl group is thereby protected. Bingham and Darrall[2] have shown that in the case of the octyl alcohols the closer the associating OH group is to the center of the chain the less is the association; and in the methyl heptanols the nearer the non-associating CH_3 group is to the associating OH group the less is the association. There is a single exception to this generalization, 4-methyl heptanol-3 being less associated at 200 rhes than 4-methyl heptanol-4. Bingham and Spooner[3] brought out the fact that the compounds having the hydroxyl group attached to the fourth carbon atom have a much higher temperature coefficient of fluidity than those having the hydroxyl group attached to the third carbon atom; and that at about 400 rhes the fluidity-temperature curves will cross. Thus it seems that the above statements do not fully apply at low temperatures.

[1] Bingham and Fornwalt, J. Rheology **1**, 372 (1930).
[2] Bingham and Darrall, J. Rheology **1**, 174 (1930).
[3] Bingham and Spooner, J. Rheology **3**, 221 (1932).

In the case of aromatic compounds, Bingham and Spooner have made several observations:

1. When two non-associating groups are attached to the benzene ring, the para compounds are less associated than the ortho compounds. They have suggested that the meta compound would have an association between that of the ortho and para compounds, but in the xylenes this is not the case, as *m*-xylene is actually less associated than *p*-xylene.
2. When the aromatic compound contains two associating groups, the para compound should be the most highly associated and the ortho compound the least. Since compounds of this type are solids at ordinary temperatures, data are lacking.
3. When the compound contains one associating and one non-associating group, such as the cresols and methyl cyclohexanones, the presence of the non-associating group in the ortho position is most effective in lowering the association, as would be expected on the basis of the theory of protection, and in the para position it is least effective. However, the toluidines, which belong to this type of compound, show an exception to this generalization, the ortho compound being slightly more highly associated than the meta and para compounds.

They have suggested the need of a systematic study of aromatic compounds, and it is for this purpose that we have undertaken this investigation.

Materials

The compounds measured were prepared in the organic laboratories of the Eastman Kodak Company, and are as follows: *o*-, *m*-, and *p*-chlorotoluene, *o*-, *m*-, and *p*-bromotoluene, *o*-, *m*-, and *p*-nitrotoluene, *o*-, *m*-, and *p*-phenetidine, and *o*-, *m*-, and *p*-bromoaniline.

The chloro-, bromo-, and ortho- and meta-nitrotoluenes were dehydrated for several days over anhydrous calcium chloride. The phenetidines were dried for several days over sodium hydroxide. Para-nitrotoluene and para-bromoaniline, which are solids melting at 51.3° and 66.4°, respectively, were dried in a desiccator for several weeks. Ortho- and meta-bromoaniline, having little affinity for water, were distilled under reduced pressure without dehydrating. Para-bromoaniline, which is easily decomposed at high temperatures, was used without distilling. All other compounds were distilled into three fractions under atmospheric pressure, and in each case the middle fraction was used for measurement.

Apparatus

The fluidities of all compounds, with the exception of *o*-chlorotoluene from 0°C to 40°C, were measured in viscometer number 1–31. This instrument was calibrated at 20°C with pure, distilled, dust-free water, a viscosity of 1.005 cp being assumed for this temperature.

For purposes of calculation in this study, we have taken $C=1.818\times10^{-7}$, $C'=0.01593$, and the hydrostatic head ($h_1=+0.01$ cm), the right limb being higher than the left. The value of $m_l=1.46$, and of $m_r=0.74$.

An explanation of these constants, a description of the instrument used and the method of measurement and calculation are given in Bingham's *Fluidity and Plasticity*, Appendix A, with supplementary information on the use of m_l and m_r in *A New Correction in Viscosity Measurements*.[4] The capillary was 10.00 cm long, and the volume of the bulbs of the viscometer was 4.00 ml.

(*o*-Chlorotoluene, from 0°C to 40°C, was measured in viscometer number 1–23, which was calibrated in a similar manner, the constants for this instrument being $C=0.9650\times10^{-7}$, $C'=0.01784$, and the hydrostatic head ($h_1=-0.30$ cm), the left limb being higher than the right.)

Densities were determined by the use of pycnometer number 1–31, calibrated at eight temperatures by means of water.[5]

Temperatures were read to hundredths of a degree on a thermometer number 36,715, calibrated at the Physikalisch Technischen Reichsanstalt and the U. S. Bureau of Standards. Stem corrections were made when necessary.

The time of flow was measured to tenths of a second on "suburban decimal" watch number 135,095, which had a correction factor of 0.9995.

Results

The fluidities and densities were measured at 0°, 10°, 20°, 30°, 40°, 60°, 80° and 100°C, except where the melting point of the compound interfered with the temperature schedule. The density of *p*-bromoaniline, the melting point of which is

[4] Bingham and Geddes, Physics **4**, 203 (1933).

[5] Bingham and Stephens, Thesis, Lafayette College, Easton, Pa. (1931).

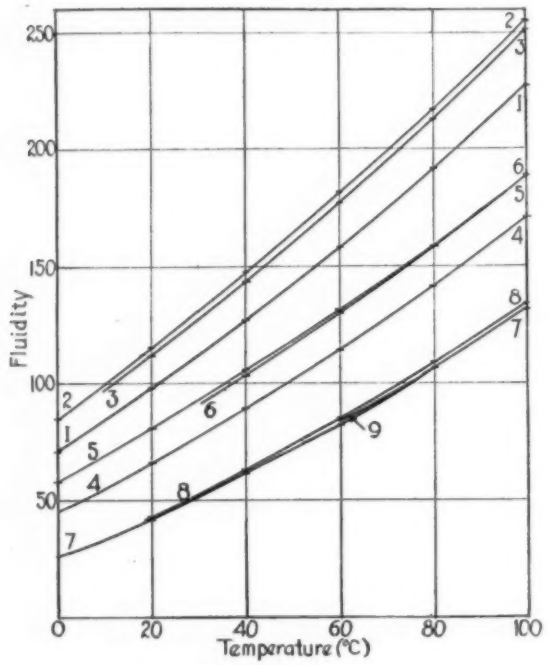


FIG. 1. Fluidity-temperature. 1. *o*-Chlorotoluene; 2. *m*-chlorotoluene; 3. *p*-chlorotoluene; 4. *o*-bromotoluene; 5. *m*-bromotoluene; 6. *p*-bromotoluene; 7. *o*-nitrotoluene; 8. *m*-nitrotoluene; 9. *p*-nitrotoluene.

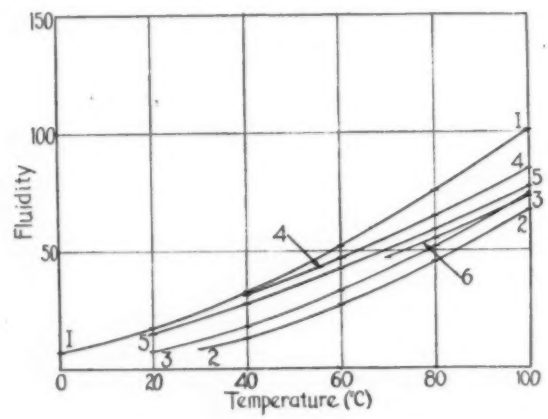


FIG. 2. Fluidity-temperature. 1. *o*-Phenetidine; *m*-phenetidine; 3. *p*-phenetidine; 4. *o*-bromoaniline; 5. *m*-bromoaniline; 6. *p*-bromoaniline.

66.4°C, was not measured because of the difficulty of introducing it into the pycnometer. Its approximate specific volume was inferred from the specific-volume, temperature curves of ortho- and meta-bromoaniline. In Table I is given a summary of the fluidities and specific volumes of the compounds at the temperatures noted above. The results are plotted in Figs. 1, 2, 3 and 4.

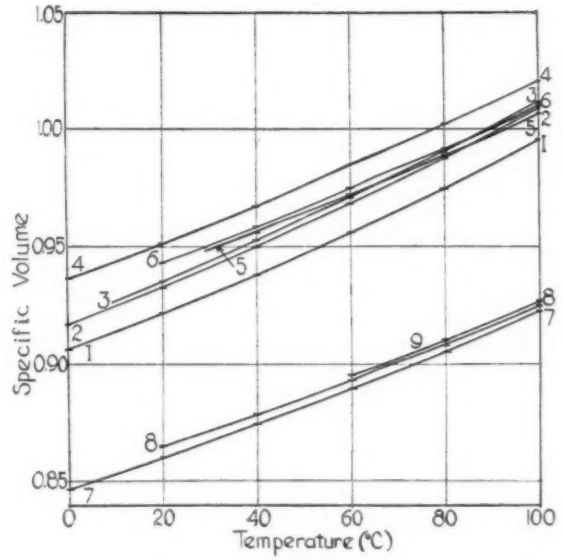


FIG. 3. Specific volume-temperature. 1. *o*-Chlorotoluene: 2. *m*-chlorotoluene; 3. *p*-chlorotoluene; 4. *o*-phenetidine; 5. *m*-phenetidine; 6. *p*-phenetidine; 7. *o*-nitrotoluene; 8. *m*-nitrotoluene; 9. *p*-nitrotoluene.

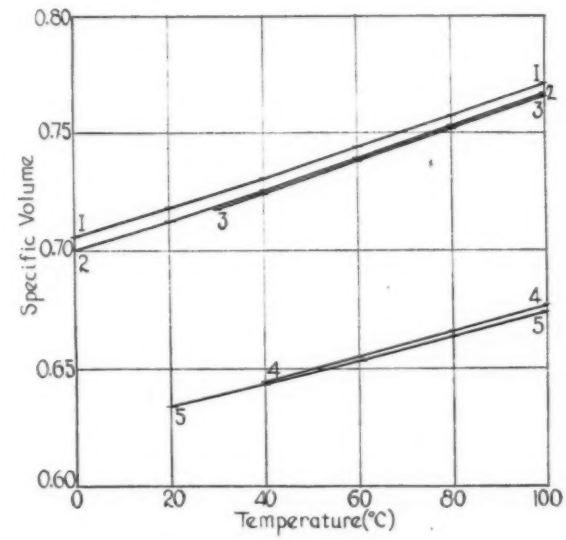


FIG. 4. Specific volume-temperature. 1. *o*-Bromotoluene; 2. *m*-bromotoluene; 3. *p*-bromotoluene; 4. *o*-bromoaniline; *m*-bromoaniline.

In the table, the column headed φ gives the fluidity in rhes; and V, the specific volume.

DISCUSSION OF RESULTS

The associations of all ortho, meta and para compounds the fluidities of which have been determined are listed in Tables II, III and IV.

TABLE I. *Summary of the fluidities and specific volumes of all compounds measured.*

Temp.	φ	V	Temp.	φ	V
	o-Chlorotoluene			*o*-Bromotoluene	
0	71.28	0.9057	0	45.29	0.7055
10	84.14	0.9135	10	55.40	0.7112
20	97.80	0.9214	20	66.14	0.7174
30	112.01	0.9291	30	77.45	0.7234
40	126.69	0.9375	40	89.36	0.7298
60	157.78	0.9558	60	114.45	0.7432
80	191.50	0.9753	80	141.63	0.7567
100	227.88	0.9952	100	170.58	0.7706
	m-Chlorotoluene			*m*-Bromotoluene	
0	84.87	0.9164	0	57.84	0.7001
10	98.83	0.9245	10	68.83	0.7058
20	114.02	0.9327	20	80.34	0.7119
30	130.88	0.9413	30	92.34	0.7180
40	146.91	0.9502	40	104.76	0.7243
60	181.23	0.9688	60	130.97	0.7376
80	217.14	0.9876	80	158.78	0.7514
100	255.11	1.0086	100	188.22	0.7660
	p-Chlorotoluene			*p*-Bromotoluene	
10	96.88	0.9264	30	91.31	0.7175
20	112.04	0.9352	40	103.72	0.7238
30	127.50	0.9438	60	130.27	0.7373
40	143.35	0.9526	80	158.73	0.7508
60	177.23	0.9713	100	188.31	0.7651
80	213.41	0.9906			
100	251.58	1.0112			
	o-Nitrotoluene			*o*-Phenetidine	
0	26.08	0.8460	0	6.058	0.9361
10	33.83	0.8530	10	10.58	0.9433
20	42.25	0.8601	20	16.45	0.9512
30	51.44	0.8672	30	23.69	0.9592
40	61.28	0.8745	40	32.02	0.9675
60	82.78	0.8900	60	51.81	0.9846
80	106.37	0.9057	80	75.03	1.0020
100	131.85	0.9223	100	100.71	1.0202
	m-Nitrotoluene			*m*-Phenetidine	
20	42.87	0.8642	30	7.738	0.9487
30	52.45	0.8712	40	12.61	0.9563
40	62.61	0.8781	60	26.33	0.9726
60	84.62	0.8934	80	44.73	0.9889
80	108.55	0.9087	100	66.75	1.0064
100	134.01	0.9246			
	p-Nitrotoluene			*p*-Phenetidine	
60	83.43	0.8959	20	7.751	0.9426
80	106.68	0.9108	30	12.05	0.9503
100	131.98	0.9266	40	17.82	0.9580
			60	32.66	0.9750
			80	51.50	0.9920
			100	73.12	1.0096
	o-Bromoaniline			*m*-Bromoaniline	
40	31.38	0.6434	20	14.69	0.6337
60	46.35	0.6543	30	20.39	0.6383
80	64.81	0.6650	40	27.06	0.6430
100	84.14	0.6760	60	41.94	0.6531
			80	58.98	0.6630
			100	76.45	0.6732
	p-Bromoaniline				
70	47.00	(0.6577)			
80	55.11	(0.6628)			
100	72.37	(0.6729)			

TABLE II. *Associations of compounds at fluidities of 50, 100 and 200 rhes.*

Substance	Association (n) at fluidity of 50 rhes	100 rhes	200 rhes
o-Chlorotoluene		1.107	1.119
m-Chlorotoluene		1.065	1.074
p-Chlorotoluene		1.071	1.081
o-Bromotoluene	(1.082)*	1.062	(1.057)
m-Bromotoluene		1.021	(1.024)
p-Bromotoluene		1.023	(1.023)
o-Nitrotoluene	1.413	1.530	
m-Nitrotoluene	1.409	1.522	
p-Nitrotoluene		1.530	
o-Phenetidine	1.545	1.608	
m-Phenetidine	1.671	(1.731)	
p-Phenetidine	1.641	(1.706)	
o-Bromoaniline	1.458	(1.502)	
m-Bromoaniline	1.482	(1.538)	
p-Bromoaniline	1.498	(1.560)	

* Values in parentheses depend upon extrapolation.

TABLE III. *Associations[3] of ortho, meta and para compounds studied previous to this research.*

Substance	Association (n) at fluidity of 50 rhes	100 rhes	200 rhes
o-Chlorophenol	(1.400)	1.372	
m-Chlorophenol	(1.545)		
p-Chlorophenol	(1.569)		
o-Cresol	1.607	1.560	
m-Cresol	1.658	1.603	
p-Cresol	1.676	1.618	
o-Toluidine	1.730	1.798	(1.831)
m-Toluidine	1.704	1.766	(1.803)
p-Toluidine	1.695	1.767	(1.840)
o-Methyl cyclohexanone	1.365	1.354	
m-Methyl cyclohexanone	1.365	1.359	
p-Methyl cyclohexanone	1.365	1.366	
o-Xylene	(1.168)	1.143	1.146
m-Xylene	(1.084)	1.063	1.073
p-Xylene	(1.110)	(1.080)	1.083
Ethyl *o*-toluidine	1.384	1.418	
Ethyl *p*-toluidine	1.414	(1.439)	

TABLE IV. *Associations of o-, m- and p-fluorine compounds at fluidities of 50, 100 and 200 rhes, studied by Swarts.*

Substance	Association (n) at fluidity of 50 rhes	100 rhes	200 rhes
o-Fluoronitrobenzene	(1.512)	(1.654)	
m-Fluoronitrobenzene	(1.483)	(1.634)	
p-Fluoronitrobenzene	(1.516)	(1.652)	
m-Difluorobenzene			1.091
p-Difluorobenzene			1.125
o-Fluoroaniline	(1.734)	(1.855)	
m-Fluoroaniline	(1.744)	(1.868)	
p-Fluoroaniline	(1.769)	(1.890)	
o-Fluorotoluene		(1.152)	1.175
m-Fluorotoluene		(1.114)	1.137
p-Fluorotoluene		(1.120)	1.147
o-Fluorophenetol	(1.226)	(1.210)	
m-Fluorophenetol	(1.196)	(1.178)	
p-Fluorophenetol	(1.201)	(1.183)	

The associations have been calculated by the method proposed by Bingham[6] from atomic-temperature constants given by Bingham and Spooner.[3] Two types of compounds are included: those containing two non-associating groups, and those containing one associating and one non-associating group.

1. In the case of the compounds measured containing two non-associating groups (the chlorotoluenes and bromotoluenes), it is seen (Table II) that at a fluidity of 100 rhes the ortho compound is the most associated, the para next, and the meta the least associated. This is analogous to the case of the xylenes, discussed in the introduction. However, it will be noted that the para compound has the higher temperature coefficient of fluidity, and the fluidity-temperature curve of *p*-chlorotoluene shows a tendency to cross that of the meta compound at higher temperatures, while the para-bromotoluene actually does cross that of the meta compound at about 99°C. *p*-Xylene, also, has a lower association at 500 rhes than *m*-xylene, although at lower fluidities it is more associated than the meta compound, thus showing that the fluidity-temperature curves cross. This behavior is very similar to that of 4-methyl heptanol-3 and 4-methyl heptanol-4, discussed in the introduction.

A consideration of the structure of these compounds suggests an explanation. In 4-methyl heptanol-4 both the non-associating methyl group and the associating hydroxyl group are as near the center of the chain as possible, so that a minimum of association might be inferred. However, it is possible that the methyl and hydroxyl attached to adjacent carbon atoms may actually get closer together, particularly at low temperatures, than would be possible if they were attached to the same carbon atom. It is a fact that the temperature coefficient of the fluidity of 4-methyl heptanol-3 is higher than that of 4-methyl heptanol-4 at low temperatures.

The same explanation finds application in the aromatic compounds, provided that the benzene ring is flexible. Two non-associating groups may at low temperatures offer less protection in the para position than in the meta position. The use of a model will most readily convince one that groups attached in the para position may by bending leave the ring exposed, but that no bending would bring about a similar approach of groups in the meta position. It is realized that an explanation may also be based upon the electrical charges upon the atoms, but it is not as easy to see why the para compound should have the higher temperature coefficient of fluidity, upon this explanation. On the other hand, it would be explained by the increased kinetic energy at the higher temperatures.

The conclusion is also borne out by the data of Swarts,[7] who found that in the case of the fluorotoluenes and fluorophenetols, compounds containing two non-associating groups and therefore belonging to this type, the fluidity was lowest in the ortho compound, next lowest in the para compound, and highest in the meta compound. Also, *m*-difluorobenzene is less associated than *p*-difluorobenzene, although data on the ortho compound are lacking. The temperatures for a fluidity of 100 rhes have been extrapolated and the associations calculated according to the method of Bingham.[6] These are listed in Table IV.

2. In the case of compounds containing one associating group and one non-associating group, according to the suggestion advanced by Bingham and Spooner,[3] we would expect the ortho compound to be the least associated, and the para compound most associated, with the meta compound occupying a middle position but in this intermediate case, much will depend upon the character of the two groups. This has already been found true in the case of the chlorophenols, cresols and methyl cyclohexanones, while *o*-ethyl toluidine is less associated than *p*-ethyl toluidine. Data on the meta compound are lacking (Table III). This research has shown that the bromoanilines, which belong to this type of compound, have associations ranging $o < m < p$ (Table II).

The data of Swarts[7] on the fluoroanilines have been extrapolated, and it has been found that they behave similarly, the ortho compound having the lowest association, and the para compound being the most associated (Table IV).

3. The nitrotoluenes, although containing one

[6] Bingham, *Fluidity and Plasticity*.

[7] Swarts, J. Chim. Phys. **28**, 622 (1931).

mildly associating and one non-associating group, behave somewhat differently. The meta compound is slightly less associated than the para compound, as would be expected, but *o*-nitrotoluene is equal to *p*-nitrotoluene in association (Table II).

This is due to the interference of the two substituted groups. In the ortho position the methyl group is protecting the nitro group but is not so effective in protecting the benzene ring, so that the ortho compound is somewhat more associated than the other two isomers. In any case, the difference is slight, the values being 1.530, 1.522 and 1.530 for *o*-, *m*- and *p*-nitrotoluene respectively, at a fluidity of 100 rhes (Table II).

The data of Swarts on the nitrofluorobenzenes, a very similar set of compounds, have been extrapolated to a fluidity of 100 rhes, and it was found that the associations are 1.654, 1.634 and 1.652 for *o*-, *m*- and *p*-nitrofluorobenzene, respectively (Table IV), the differences here also being very slight and practically identical with the findings in the case of the nitrotoluenes.

4. The phenetidines contain NH_2, a highly associating group, and OC_2H_5, which is practically a neutral group, being next below H in association (Table VI). The associations range in exactly the opposite order from those of the compounds containing two non-associating groups, as seen by inspection of Table II. The meta compound is the most associated, the para next, with ortho-phenetidine having the lowest association of the three. As in the case of compounds containing two non-associating groups, the fluidity-temperature curve of the para compound shows a tendency to cross that of the meta compound, so that at higher temperatures, the para compound would be the most associated, as is the case with the chlorophenols, cresols, methyl cyclohexanones, bromoanilines and fluoroanilines. However, it is difficult to predict the associations of this type of compound, since the different groups may have an effect on each other as well as on the benzene ring (cf. 3, the nitrotoluenes and nitrofluorobenzenes).

TABLE V. *Boiling points*[8] *of ortho, meta and para compounds containing two associating groups.*

Compound	Formula	Boiling point (°C) of Ortho	Meta	Para
Phenylphenol	$C_6H_5C_6H_4OH$	275°	>300°	308°
Nitrodiphenyl	$C_6H_5C_6H_4NO_2$	320°		340°
Aminoacetophenone	$NH_2C_6H_4COCH_3$	252°	s.d.290°	295°
Methyl nitrobenzoate	$NO_2C_6H_4COOCH_3$	269°	279°	
Dihydroxybenzene	OHC_6H_4OH	245° ($o-o'$)	276.5°	286.2° ($o-p'$)
Diphenol	$OHC_6H_4C_6H_4OH$	326°		342°

5. In the case of the toluidines, where there is one associating NH_2 group and one non-associating CH_3 group, it is seen that at 50 rhes the associations run $p<m<o$, at 100 rhes, $m<p<o$, and at 200 rhes, $m<o<p$ (Table III). Thus the fluidity-temperature curve of the para compound crosses both that of the meta and the ortho compound. Each of these compounds was measured by a different investigator, and the para compound by three separate investigators, each of whom provided a small section of the curve. Further investigation on this set of isomers should be undertaken before any conclusion is reached.

APPENDIX

Summary

(1) The atomic-temperature constants of fluorine at fluidities of 50, 100, 200 and 300 rhes have been calculated, using 1,1,2-trichloro-1,2,2-trifluoroethane as the best available compound.

(2) By using these atomic-temperature constants, and those of C, H, O, Cl, Br and N given by Bingham and Spooner,[3] the associations of 23 fluorine compounds have been calculated at one or more fluidities (Table VIII).

(3) On the basis of the theory of protection, and taking into account the associative effect due to the electrostatic attraction and repulsion of charged atoms, the effect of the introduction of fluorine atoms on the associations of these 23 compounds has been explained. The fluorine compounds thus afford strong supporting evidence for the theory of protection and for the usefulness of the fluidity method for determining association.

During the course of this research, we were fortunate in having made available, through publication, the data of F. Swarts.[7] They consisted of the fluidities of 37 organic fluorine compounds, at temperatures ranging in general from 20°C to 60°C, and included four complete sets of ortho, meta and para compounds, these being the fluorotoluenes, nitrofluorobenzenes, fluoroanilines and fluorophenetols. Also, data on meta- and para-difluorobenzene were given. These data have already been considered. Of the remainder, 3 were ring compounds—fluorobenzene, trifluoro-

[8] International Critical Tables.

toluene and trifluoromethyl cyclohexane—the other 20 being aliphatic compounds.

It is proposed here to examine these results also on the basis of the theory of protection.

Swarts has compared his results by two methods. The first consists in comparing the differences in the fluidities at equal temperatures. This has the disadvantage that the comparison is not made under truly comparable conditions, which should be at temperatures of equal fluidities.[6] By the second method, he compares the differences in the temperatures for equal fluidities. Neither method gives the readily comparable values of the association. It merely requires the division of the observed temperature of each compound by the calculated temperature for that fluidity, in order to obtain a comparison of the associations of the compounds.[6] The comparison of associations has the very great advantage that it enables one to examine constitutive influences without the effects of varying molecular weights entering into the comparison.

In order to show which groups are associating and which are non-associating, Table VI is introduced. With benzene for reference, those groups which result in an increase in association (above benzene in the table) are associating groups, and those which result in a decrease in association (below benzene in the table) are non-associating groups.

TABLE VI. *Association of benzene and substituted-benzene derivatives at a fluidity of 100 rhes.*

Compound	Substituted group	n*
Aniline	NH_2	1.971
Phenol	OH	(1.705)
Nitrobenzene	NO_2	1.625
Phenyl cyanide	CN	1.557
Benzene	(H)	1.284
Phenyl ethyl ether	OC_2H_5	1.188
Fluorobenzene	F	(1.182)
Toluene	CH_3	(1.139)
Chlorobenzene	Cl	1.115
Bromobenzene	Br	1.063
Iodobenzene	I	1.041

* (All associations given are those calculated by Bingham and Spooner,[3] except that of fluorobenzene, which was calculated by the authors.)

To obtain the association of fluorobenzene, it was first necessary to obtain the atomic-temperature constant of the fluorine atom. Swarts gives a value of 61.3, which he obtained by adding 2.1 to the value of the hydrogen atom, this figure (2.1) being the difference in the temperature, for a fluidity of 200 rhes, observed by substituting a fluorine atom for a hydrogen atom. This method, however, does not take into account the difference in association caused by a substituted halogen, so that for purposes of calculation in this study, the atomic-temperature constant of the fluorine atom has been redetermined, using 1,1,2-trifluoro-1,2,2-trichloroethane as the best available compound (cf. 6, this discussion). In Table VII it is shown how these values are obtained.

TABLE VII. *Determination of atomic-temperature constants of fluorine at fluidities of 50, 100, 200 and 300 rhes.*

Fluidity	1, 1, 2-Trifluoro-1, 2, 2-trichloroethane		F
300	From extrapolation of the fluidity-atomic temperature curve		(71.5)
200	Obs. temp.	321.0	
	C_2Cl_3	134.9	
	3F	186.1	62.0
100	Obs. temp.	(286.5)	
	C_2Cl_3	105.1	
	3F	(163.4)	(54.5)
50	Obs. temp.	(237.0)	
	C_2Cl_3	82.9	
	3F	(154.1)	(51.4)

With these values of F, and the values of C, H, O, Br, Cl and N given by Bingham and Spooner, the associations of the compounds determined by Swarts have been calculated, as completely as possible, at fluidities of 50, 100, 200 and 300 rhes (Table VIII). Associations of ortho, meta and para fluorine compounds are listed in Table IV.

In order to test the data on the basis of the theory of protection, the effect of introducing halogen atoms into organic compounds may first be predicted, according to the theory.

TABLE VIII. *Associations of organic fluorine compounds at fluidities of 50, 100 and 200 rhes (see also Table IV).*

Substance	Association (n) at fluidity at 50 rhes	100 rhes	200 rhes
1,1,2-Trichloro-1,2,2-trifluoroethane	(1.000)	(1.000)	1.000
Trifluoroacetic acid		(1.619)	1.706
1,1-Dichloro-2,2-difluoroethane			1.202
1,1,2-Trichloro-2-fluoroethane			1.143
Difluoroacetic acid		(2.033)	
1-Bromo-2,2-difluoroethane			1.239
2,2-Difluoroethyl alcohol			(2.100)
2-Fluoroethyl alcohol			(2.104)
1,1,1-Trifluoroacetone			(1.244 at 300 rhes)
1,1,1-Trifluoroisopropyl alcohol		(1.817)	
Ethyl trifluoroacetate			1.175
1,1-Difluoroethyl acetate			1.490
Ethyl difluoroacetate			1.383
1-Fluoroethyl acetate			1.509
Ethyl fluoroacetate			1.465
1,1,1-Trifluoro-*tert.*-butyl alcohol		(1.687)	
1,1,1-Trifluoroisopropyl acetate			1.228
n-Amyl fluoride			(1.168 at 300 rhes)
Fluorobenzene		(1.182)	1.221
2,5-Difluoroaniline		(1.795)	
Benzotrifluoride			1.101
Trifluoromethyl cyclohexane		(1.215)	
n-Heptyl fluoride			1.145

Postulates

1. (A) All the halogens, including fluorine, are to be considered as non-associating groups, with respect to hydrogen (Table VI). However, since the halogens are electronegative and hydrogen is electropositive, the attraction of these atoms for one another, when connected to the same carbon atom, must be taken into account.

(B) Considering methane, the carbon atom is surrounded by four strongly electropositive groups, repelling each other, and also other methane molecules, thus having little tendency toward association.

(C) Upon introducing a halogen into the compound, the carbon atom is surrounded by three electropositive hydrogens and one electronegative halogen, so that even though the halogen is a slightly better protective atom than hydrogen, the attraction of the opposing charges for each other, and for other methyl halide molecules, results in an increase in association.

(D) Upon introducing a second halogen into the compound, the carbon is surrounded by two positive hydrogens and two negative halogens, so that all the surrounding groups have an attraction for one another, and thus the association of the compound is still further increased.

(E) Upon introducing a third halogen into the compound, the carbon is surrounded by one positive hydrogen and three negative halogens, so that there is less attraction of the surrounding groups for each other or for other like molecules than when only two halogens were substituted. Considering that the hydrogen atom and one halogen atom neutralize each other, it is seen that the carbon is left protected by two halogen atoms in the case of the tri-halogen substituted methane, whereas in the case of the mono-halogen substituted methane, the carbon atom is protected by two hydrogen atoms. Since, by postulate (1A), halogens are considered as non-associating groups with respect to hydrogen, the tri-halogen substituted compound should have a somewhat lower association than the mono-halogen substituted compound.

(F) Upon introducing the fourth halogen atom, the carbon is surrounded by four strongly electronegative groups, mutually repelling, and repelling other molecules. Therefore, the compound is well-protected, and, since by postulate (1A) halogens are more protecting than hydrogen, the tetra-substituted compound should be less associated than the original methane.

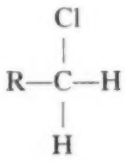
Data on the hydrocarbons[3] show that the associations of members of this series are close to unity, although the value for methane is lacking, as is that of methyl chloride. However, the associations of di-, tri- and tetrachloromethane follow the predictions above (Table IX).

TABLE IX. *Association of di-, tri- and tetrachlor-substituted methanes at 200 rhes.*

Substance	Formula	n
Methylene chloride	CH_2Cl_2	1.161
Chloroform	$CHCl_3$	1.049
Carbon tetrachloride	CCl_4	1.018

2. (A) Then, to extend the theory to include compounds with two or more carbon atoms, where at most three hydrogens are attached to

the same carbon atom, it is obvious that the substitution of one halogen will increase the association, tying up one of the hydrogens, and leaving the carbon atom protected by the radical R and one H (cf. (1C)).



(B) The substitution of the second halogen atom will result in the protection of the carbon atom by the radical R and a halogen (Cl). By postulate (1A), this will have a lower association than the mono-halogen-substituted compound but, of course, a higher association than the non-substituted compound (cf. (1E)).

(C) The substitution of the third halogen atom results in the protection of the carbon atom by three strongly electronegative groups, with no attraction for one another, so that this compound is well-protected and will have an association less than that of the non-halogen-substituted compound (cf. (1F)).

The data of Swarts were made use of to test these conclusions.

1. The monofluoroethyl acetates should have considerably higher association than ethyl acetate (2A); the difluoroethyl acetates should have an association higher than ethyl acetate but lower than the monofluoroethyl acetates (2B); the trifluoroethyl acetates should have the lowest association of any of these compounds, even lower than that of ethyl acetate itself (2C). Table X shows the correctness of the predictions.

TABLE X. *Association of ethyl acetate*[3] *and substituted-fluorine derivatives at 200 rhes.*

Substance	Formula	n
Ethyl acetate	$CH_3COOC_2H_5$	1.232
Ethyl fluoroacetate	$CH_2FCOOC_2H_5$	1.465
1-Fluoroethyl acetate	$CH_3COOCH_2CH_2F$	1.509
Ethyl difluoroacetate	$CHF_2COOC_2H_5$	1.383
1,1-Difluoroethyl acetate	$CH_3COOCH_2CHF_2$	1.490
Ethyl trifluoroacetate	$CF_3COOC_2H_5$	1.175

It will also be noted that the association of the ethyl fluoroacetates, where the protective fluorine atom is close to the associating carboxyl group, is lower than the association of the fluoroethyl acetates, where the protective fluorine atom is farther removed.

2. Similarly, monofluoroacetic acid should have an association considerably above that of acetic acid (2A); difluoroacetic acid should be more associated than acetic acid but somewhat less than monofluoroacetic acid (2B); trifluoroacetic acid should have a lower association than acetic acid or the mono- and difluoroacetic acids (2C). Although data on monofluoroacetic acid are lacking, Table XI shows that these other expectations are realized.

TABLE XI. *Association of acetic,*[3] *difluoroacetic and trifluoroacetic acids at 100 rhes.*

Substance	Formula	n
Acetic acid	CH_3COOH	1.868
Difluoroacetic acid	CHF_2COOH	(2.023)
Trifluoroacetic acid	CF_3COOH	(1.619)

3. Monofluoroethyl alcohol should have an association greater than that of difluoroethyl alcohol (2B), which should be more associated than ethyl alcohol (2B), which in turn should be more associated than trifluoroethyl alcohol (2C). Although in this case, data on trifluoroethyl alcohol are lacking, the other expectations accord with the facts (Table XII).

TABLE XII. *Association of ethyl,*[3] *2-fluoroethyl and 2,2-difluoroethyl alcohols at 200 rhes.*

Substance	Formula	n
Ethyl alcohol	CH_3CH_2OH	(1.969)
2-Fluoroethyl alcohol	CH_2FCH_2OH	(2.104)
2,2-Difluoroethyl alcohol	CHF_2CH_2OH	(2.100)

4. Data are also given on 1,1,1-trifluoroisopropyl and 1,1,1-trifluoro-*tert.*-butyl alcohols. Both these compounds would be expected to have associations considerably lower than the non-substituted alcohols (2C). Table XIII verifies this.

5. The association of benzotrifluoride is somewhat lower than that of toluene (Table XIV), as would be expected, since the substitution of three halogen atoms in a methyl group reduces the association of the compound (2C).

TABLE XIII. *Association of isopropyl,[3] tertiary-butyl,[3] 1,1,1-trifluoroisopropyl and 1,1,1-trifluoro-*tert.*-butyl alcohols at 100 rhes.*

Substance	Formula	n
Isopropyl alcohol	$(CH_3)_2CHOH$	1.927
1,1,1-Trifluoroisopropyl alcohol	$(CH_3)(CF_3)CHOH$	(1.817)
Tertiary butyl alcohol	$(CH_3)_3COH$	1.796
1,1,1-Trifluoro-*tert.*-butyl alcohol	$(CH_3)_2(CF_3)COH$	(1.687)

TABLE XIV. *Association of toluene and benzotrifluoride at 200 rhes.*

Substance	Formula	n
Toluene	$C_6H_5CH_3$	1.139
Benzotrifluoride	$C_6H_5CF_3$	1.101

6. It is evident that the association of 1,1,2-trifluoro-1,2,2-trichloroethane would be very close to unity, since the carbon atoms are fully protected by six non-associating groups, all strongly electronegative, repelling one another and also the surrounding molecules. It is for this reason that this has been taken to be the best available compound for the calculation of the atomic-temperature constant of fluorine, with the temporary working assumption that its association is unity.

7. The association of 1-fluoro-1,2,2-trichloroethane would be expected to be slightly greater than that of 1,1,2,2-tetrachloroethane, and the association of 1,1-difluoro-2,2-dichloroethane should be higher than either of these compounds, since fluorine is not quite so good a protective group as chlorine (Table VI), and therefore, the substitution of fluorine atoms for chlorine atoms would increase the association (Table XV).

8. Although no definite basis of comparison exists for the compound CH_2BrCHF_2, its association of 1.239 at a fluidity of 200 rhes appears to be reasonable on the basis of the theory, since, although bromine is less associating than chlorine

TABLE XV. *Association of tetra-halogen-substituted ethanes at 200 rhes.*

Substance	Formula	n
1,1,2,2-Tetrachloroethane	$CHCl_2CHCl_2$	(1.079)[3]
1-Fluoro-1,2,2-trichloroethane	$CHFClCHCl_2$	1.143
1,1-Difluoro-2,2-dichloroethane	CHF_2CHCl_2	1.202

(Table VI), the fact that one carbon atom has only one halogen attached to it would make the association of this compound higher than if two halogens were attached to each carbon atom (2B), as is the case in 1,1-difluoro-2,2-dichloroethane, the association of which is 1.202.

9. Alkyl monofluorides should have associations larger than the corresponding hydrocarbons (2A). Swarts studied two of this type of compound, *n*-amyl fluoride and *n*-heptyl fluoride. The associations of these are compared with those of pentane and heptane in Table XVI.

TABLE XVI. *Association of pentane, heptane, n-amyl fluoride and n-heptyl fluoride.*

Substance	Formula	n $\varphi=200$	$\varphi=300$
Pentane	C_5H_{12}		1.005
n-Amyl fluoride	$C_5H_{11}F$		(1.168)
Heptane	C_7H_{16}	1.028	
n-Heptyl fluoride	$C_7H_{15}F$	1.145	

10. The association of trifluoroacetone should be less than that of acetone (2C) (cf. 4, 5). This is also found to be the case, the associations at a fluidity of 300 rhes being 1.314 for acetone, and (1.243) for 1,1,1-trifluoroacetone, although the latter value is somewhat in doubt, due to the uncertainty of the atomic-temperature constant of fluorine at 300 rhes.

11. Although no compound is directly suitable for comparison with trifluoroisopropyl acetate, its association of 1.228 at 100 rhes is within the range of associations covered by the isomers of isopropyl acetate, from methyl isobutyrate with $n=1.174$ to *n*-butyl formate with $n=1.261$.

12. The associations of the ortho-, meta- and para-fluorine compounds are treated in the main part of this paper, all being found to agree closely with the corresponding chlorine and bromine compounds and behaving according to the theory.

13. Difluoroaniline would be expected to have an association considerably less than that of aniline and also less than any of the three monofluoroanilines, since fluorine is a non-associating group (Table VI). This prediction is seen to be true by inspection of Table XVII.

TABLE XVII. *Association of aniline[3] and fluorine-substituted anilines at 100 rhes.*

Substance	n
Aniline	1.971
o-Fluoroaniline	(1.855)
m-Fluoroaniline	(1.868)
p-Fluoroaniline	(1.890)
2,5-Difluoroaniline	(1.795)

14. The association of trifluoromethyl cyclohexane would be relatively hard to determine from the constitution, since two opposing effects enter. First, the substitution of the fluorine atoms in the ring should cut down the association (Table VI). Second, the introduction of electronegative fluorine atoms which also have electropositive atoms attached, should reduce the protection (2A) and result in increased association of the compound. In this case, the opposing effects almost balance, the association of methyl cyclohexane at 100 rhes being 1.200 and that of trifluoromethyl cyclohexane being (1.215).

Conclusions

1. The fluorine atom is a protective group, being less associating than hydrogen but more associating than chlorine.

2. The atomic-temperature constants of fluorine at various fluidities are:

φ	Atomic-temperature constant
50	(51.4)
100	(54.5)
200	62.0
300	(71.5)

3. Due to their strongly electronegative character, the substitution of fluorine (and chlorine, bromine and iodine) atoms on to carbon atoms which also have electropositive hydrogen attached, results in an increase in association, caused by the attraction of the opposing charges for each other, in spite of the fact that the fluorine atom is a protective group.

4. The substitution of fluorine atoms on to carbon atoms which have no hydrogen atoms attached, results in a decrease in association.

5. Likewise, the substitution of fluorine atoms for all the hydrogens attached to a carbon atom results in a decrease in association.

The Stress-Strain Relation in Textile Fibers

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Stress-strain relations for eight common textile fibers are given (four rayons, silk, wool, cotton and ramie) under known humidity conditions. The method has two novel features: (1) In each experiment the section area was determined on the specific fiber under test, (2) the elongations were made in steps, with a relaxation interval of 30 seconds between stress observations, rather than at a constant rate which is the usual practice. The rayons exhibit an accurately linear initial curve from which Young's modulus can be determined, followed by a yield point and a long region of plastic flow. The curves for cotton and ramie are linear with no plastic yield in the range examined. In silk and wool there is no proportionality between stress and strain. Cellulose acetate exhibits the phenomena of "cold working" and marked increase of total and elastic energy with falling relative humidity. The application of Maxwell's relaxation equation is examined.

INTRODUCTION

THE textile fibers form a large and important class of materials in which rheological phenomena are of considerable interest. A complete description of their mechanical behavior, under various conditions of moisture and other vapor adsorption and of temperature, awaits the accumulation of a large amount of data. Considerable work has already been done in the field. The practical mill man is interested in the elongation and strength at the breaking point as well as the extent of recovery after elongation at known conditions of moisture content (regain). Several types of single fiber testing instruments with special arrangements for ease and rapidity of operation are in daily use.[1, 2, 3, 4] Fundamental studies have been made[5, 6, 7] by using sensitive apparatus specially designed for securing precise data on the whole course of the stress-strain relation and on flow and relaxation phenomena. All these studies are subject to serious objection in that stress estimation was made from a cross-sectional area chosen as typical of the kind of fiber used, rather than on the specific single filament under test. The resulting uncertainty in stress estimation was partially compensated for by taking an average of a large number of tests. In the present experiments the section area was measured on the tested fiber near the stressed portion. The present method also differs from previous work in the loading process. The usual procedure is to pull one end of the fiber at a constant speed. Here the stretching is made in steps. The constant rate of pull method seems open to the objection that flow phenomena, which are always present in tensioned fibers even under low stress, obscure some of the details of the stress-strain relation.

APPARATUS

The apparatus is quite simple (Fig. 1). An accurate screw with its axis vertical moves a slide to which the lower end of the fiber is attached. The upper end of the fiber pulls a lever which twists a pair of parallel horizontal wires. The rotation of the lever is measured optically by telescope and scale. The lever and twisted wire mechanism or tension gauge was directly calibrated by placing weights on a pan attached to

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[6] Harold de Witt Smith, J. Text. Inst. **22**, 158–169 (1931).

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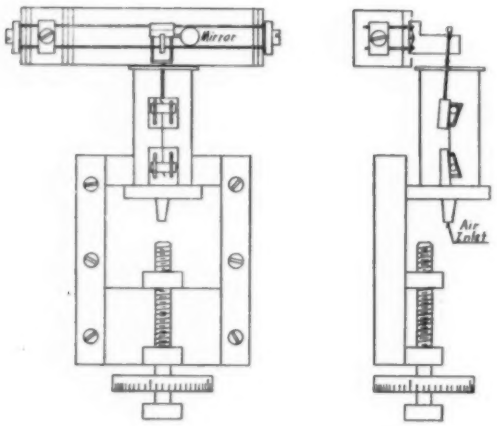


FIG. 1. Diagram of apparatus.

the lever. The scale deflection is an accurately linear function of the weights added and is free from hysteresis. The loading rate is 0.6 gram weight per centimeter scale reading. A direct determination of the fall of the lever end (i.e., the upper end of the fiber) per cm tension gauge reading was made and found to be 1.64×10^{-2} mm per cm. This amount must be subtracted from each screw setting to get the net fiber elongation. Both ends of the fiber move when the screw is moved. The net elongation is the difference in displacement of the fiber ends.

SECTION AREA MEASUREMENT

The fiber was mounted and sectioned in paraffin by Schwarz's[8] method which was further developed by G. G. Osborne (Textile Foundation Research Fellow) and the writer to adapt it to single fiber manipulation. The successful use of the technique depends upon attention to many details which will be fully described in communications to be released later by the Textile Foundation. Suffice it to say that the section area can be determined, under controlled humidity conditions, at a point removed not more than 5 mm from the length tested.

HUMIDITY CONTROL

The tensile properties of textile fibers are sensitive to adsorbed vapors the most important of which is water. It is essential that moisture conditions be accurately known. Air of any desired relative humidity (R. H.) was secured by passing it through sulfuric acid solutions of the proper density according to the technique of Wilson.[9] During tensile test the treated air was led through a glass mantle surrounding the stretched fiber in the manner used by Smith.[6] With the exception of the last three runs on celanese (cellulose acetate) (Figs. 10, 11, 12), the section areas were measured at approximately the room humidities recorded on the charts. Presumably each type of fiber will present a characteristic relation between R. H. and size of section area. An independent investigation, to be published later, established the fact that in celanese the size of section area is approximately proportional to the percent R. H. of the atmosphere surrounding the fiber. For each humidity, equilibrium conditions obtained before the area was measured. The fiber had reached a stationary size at the particular R. H. before the area was measured. In celanese the area of section at 100 percent R. H. is 14.5 percent greater than it is in the dry condition. It is logical to compute stresses on the basis of the dry area. This has been done in the case of curves 10, 11, 12.

PROCEDURE

The fiber is mounted in clamps. The upper one is hung on the tension gauge lever. The lower one is rigidly fixed to the screw slide. The initial length (L_0) is determined with a cathetometer when the fiber is pulled taut enough to give just perceptible deflection of the tension gauge except in the case of Merino wool. In this case it was necessary to put on enough stress to straighten out the many kinks characteristic of this fiber before determining L_0. L_0 should be made as small as skill and patience will permit in order to avoid, as far as possible, the weakening effect of chance injuries. (Reference 4, page 16.) In the later experiments L_0 had been reduced to about 1.5 cm. Before measuring L_0, air of the proper R. H. should be led through the glass mantle for at least one hour. The experiment on celanese mentioned above showed that section size reaches a stationary value after about one hour exposure. Presumably the other mechanical properties will

[8] E. R. Schwarz, Text. World, September 28, 1929.

[9] R. E. Wilson, J. Ind. Eng. Chem., p. 326, July, 1921.

not take a much longer time to become stationary. During the experiment proper, the lower clamp is moved downward by equal displacement increments once every 30 seconds by rapid manual turning of the screw. At the end of each 30 second interval the tension gauge is read immediately preceding the next extension. The displacement increments were 5 or 10×10^{-2} mm. The accompanying elongation increments varied between 0.1 and 0.5 percent. The time interval between any two adjacent points on each chart is 30 seconds. The increment of percent elongation is not constant throughout any given experiment because the upper clamp moves by amounts dependent upon the character of the stress-strain curve. Extension at constant load can be observed in the textile fibers even at very small stress[10] provided one waits long enough. The rate of extension or flow at constant load decreases with time.[7] In the present experiments the load itself rapidly decreases with time; hence, the rate of flow quickly becomes negligible, except where pronounced plastic flow is present, and the internal stresses are in equilibrium with the tension gauge reaction. The rate at which the reaction falls is 31.6 grams weight per mm. The tension gauge is thus much stiffer than the strongest fiber examined, namely ramie which extends at the rate of 8.05 g wt. per mm. Very consistent results have been obtained with this procedure. The results permit quantitative comparison between curves.

Discussion of Results

In addition to the 8 simple stress-strain curves at 54.8 percent R. H. (Figs. 2 to 9) there are three charts for celanese (Figs. 10, 11, 12) in which the stress was released to zero and raised again in several cycles.

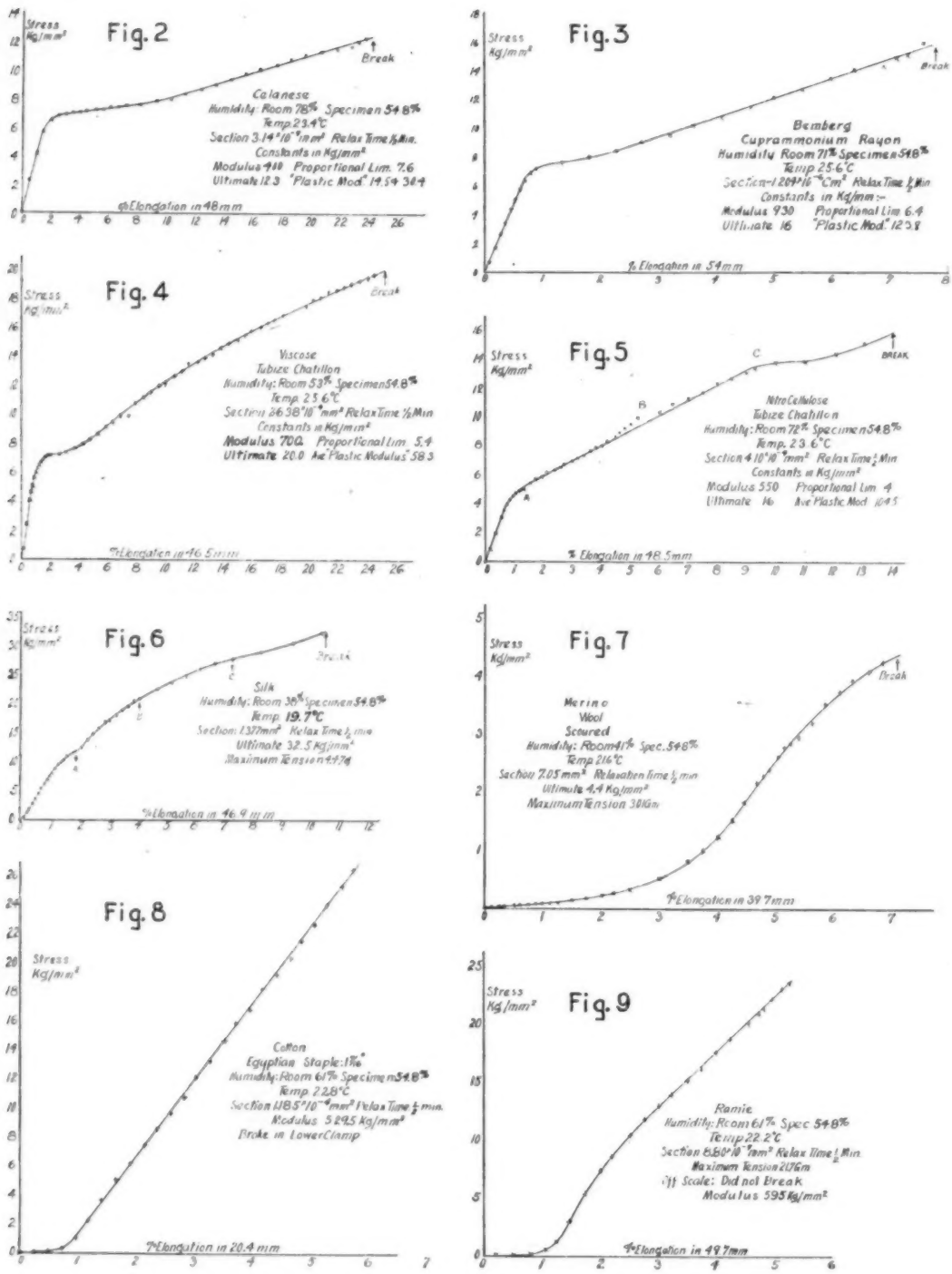
According to the type of stress-strain curve the fibers fall into three classes; (1) regenerated cellulose or cellulose derivatives (i.e., rayon); (2) fibers of animal origin (the protein fibers, silk and wool) and (3) the natural cellulose fibers, cotton and ramie. In the rayons the form of the stress-strain relation is not greatly different from that of the ordinary metals. There is an initial straight portion from which Young's modulus can be determined with considerable precision. Next, there is a narrow region of stress where elongation changes quite sharply from the slow flow characteristic of small stresses to plastic flow of a much greater magnitude in which permanent set has its origin. The Young's modulus determined from the linear portion is different for each of the rayons and is characteristic of the type of specimen.

The animal fibers do not exhibit a linear region. The curvature is continuous except for the breaks marked *A*, *B*, *C*, on the silk curve. These are due to arbitrary increases of elongation interval which were introduced in order to cut down the number of observations. The same applies to nitrocellulose. The plastic performance is a function of the procedure. The low initial slope of the wool curve is partly due to the influence of kinks which are very pronounced in Merino wool. The ultimate strength of silk, 32.5 kg/mm^2 or 4.47 grams fiber tension, is much greater than that of any of the artificial fibers of which viscose is the strongest breaking at 20 kg/mm^2. The ultimate strength of wool is the lowest of the lot, being 4.4 kg/mm^2 at a maximum fiber load of 3.01 grams.

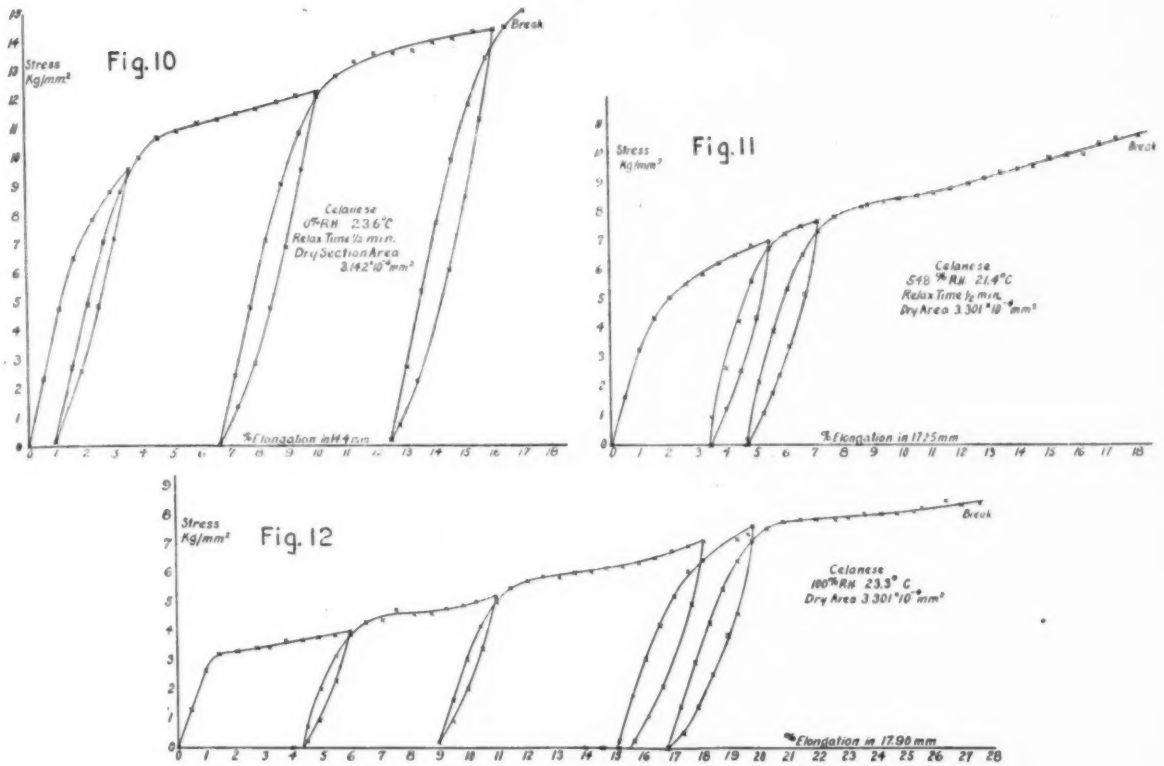
Cotton is remarkable (Fig. 8) in that the stress-strain plot is accurately linear for its entire course. The bend at low stress is due to the straightening out of the kinks as in the case of wool. This is one of four attempts to get a complete curve in the expectation that the fiber would finally exhibit a measurable plastic flow. In each case the fiber either slipped or broke in one of the clamps. Breaking in the clamps was a rare occurrence, but when it did happen the data were discarded except in the case of cotton. At medium humidities cotton is hard and tough and presents a hard, smooth surface difficult to hold in a clamping device. The rayons behave similarly under conditions approaching complete dryness. This behavior has forced the improvement of the clamps to prevent slipping. Future experiments are expected to give the complete curve for cotton.

Only part of the ramie curve is shown. The fiber will support a very large pure tension load because of great intrinsic strength as well as large section area. The tension gauge was pulled off scale before the fiber broke. The indications are

[10] Henry Green, Am. Dyestuff Reptr. **3**, 83 (1932).



FIGS. 2 TO 9. Simple stress-strain curves for various fibers at 54.8 percent relative humidity.



FIGS. 10, 11, 12. Stress-strain relations for celanese when the stress is released to 0 and raised again in several cycles.

that future experiments will show ramie to be similar to cotton.

Curves 10, 11, 12 are stress-strain relations in cellulose acetate fiber at three humidities 0, 54.8 and 100 percent. In each case the fiber was extended into the plastic flow region. The stress was then released to zero and then immediately raised again until further flow set in. The cycle was repeated several times at each R. H. as indicated on the charts. The improved section-measuring technique was used and stresses were computed on the basis of the dry section area. Ordinate differences between curves accurately represent stress differences. The curves exhibit the form characteristic of metals during the process of cold working. The total energy and elastic energy (reference 4, page 31) increase greatly with falling R. H. The range of elastic strength is greatly enhanced by previous flow. This is attributed to orientation of the micelles parallel to the tension axis,[11] the micelles remaining intact. The same type of curve, obtained with metals, is due to limited slip within the crystallites at first along planes of maximum shear stress. The crystal grains do not turn bodily.

Karger and Schmid[5] using a constant velocity of elongation did not find an accurately linear initial portion of the stress-strain curve from which Young's modulus could be determined. They used the slope of the return or unloading curve. It is quite clear from Figs. 10, 11, 12 that the modulus as determined by the two methods is approximately the same. The median lines of the hysteresis loops are approximately parallel to the initial linear part.

The third hysteresis loop in Fig. 12 at 100 percent R. H. is open at the bottom. The apparatus was accidentally jarred during the run. The tension gauge zero was knocked out of its initial setting by an amount which could not be determined until after final termination of the run. Consequently, in returning to zero in the third loop the setting for zero stress was overshot

[11] G. L. Clark, Ind. and Eng. Chem. **22**, 474 (1930).

considerably. The opening at the bottom represents the relaxation of the fiber by about 0.5 percent elongation during the time (about 4 minutes) when the tension was entirely removed.

Conclusions

Attempts have been made to explain flow phenomena in plastic materials from Maxwell's point of view.[12] He gave the expression

$$dT/dt = c(dE/dt) - T/t_r$$

for the rate of change of tension (T) in a plastic material extended at the rate (dE/dt). It may be well to test the application of the equation in the present case. Writing the equation in terms of unit stress (s) where (a) is the section area, we have

$$ds/dt = (c/a)(dE/dt) - s/t_r. \qquad (1)$$

The relaxation time (t_r), for the simplest possible behavior of the material, should be a constant but actually it appears to be a function of both stress and strain. The relaxation time on the stress-strain charts is not t_r but is arbitrarily set at the value 30 seconds while t_r is the time required for the stress to fall the fractional amount $1/e$ when the elongation is held at a constant value. If the material is suddenly extended and held at a constant elongation (dE/dt) is zero, except for the initial accelerating period, and the solution becomes

$$s = S_0 e^{-t/t_r}.$$

The stress falls exponentially with time from its initial value (S_0). Within any time interval (Δt) Eq. (1) can also be solved in the present case if certain assumptions are made as to experimental procedure. Let Fig. 13 schematically represent conditions during the two first time intervals. Let the spring (i.e., the tension gauge) be given a displacement (u_0) while the fiber is held at its slack length (L_0). At $t=0$ release the end (B) of the fiber, (A) being fixed at all times. The fiber stress will then be

$$S_1 = ku_0/a.$$

Where (k) is the elastic constant of the spring.

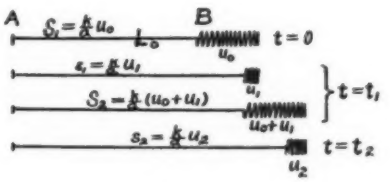


Fig. 13.

At the end of the time interval $\Delta t = t_1$ the stress will have fallen to the value

$$s_1 = ku_1/a,$$

where (u_1) is the residual displacement in the spring. At $t=t_1$ the spring is again instantaneously extended to the value u_0+u_1 when the fiber stress is

$$S_2 = k(u_0+u_1)/a.$$

After the lapse of the second time interval (Δt), (i.e., at $t=t_2$) the stress will again have fallen but this time to

$$s_2 = ku_2/a,$$

where (u_2) is the residual spring extension at the end of the second time interval. The total extension of the fiber at the end of the nth interval will be

$$E_n = (nu_0 - u_n)$$

and the corresponding stress will be

$$s_n = ku_n/a.$$

This is not the precise procedure followed. However, the apparatus could be so modified as to approximate it. The resulting stress-strain curves would probably be the same as those submitted. The amount of motion given to the screw at each reading is exactly (u_0). In the first time interval the extension

$$E = u_0 - u$$

and the stress

$$s = ku/a.$$

Therefore,

$$s = k(u_0 - E)/a$$

and

$$ds/dt = -(k/a)dE/dt.$$

Eq. (1) then becomes

$$ds/dt = -(c/k)(ds/dt) - s/t_r$$

[12] J. C. Maxwell, Phil. Mag. **35**, 134 (1868).

with the solution

$$s = S_1 e^{-t/t_r(1+c/k)}.$$

Let

$$t_r(1+c/k) = t_r',$$

which will be the relaxation time of the system as a whole. At the end of the first time interval the stress is therefore

$$s_1 = S_1 e^{-\Delta t/t_r'}.$$

At the end of the second time interval the instantaneous total stress is

$$s_2 = (S_1 + s_1)e^{-\Delta t/t_r'}$$

$$= S_1 e^{-\Delta t/t_r'} + S_1 e^{-2\Delta t/t_r'}$$

on the assumption that it is the total stress existing at any instant which decays with time. Then at the end of the nth interval

$$s_n = S_1(e^{-\Delta t/t_r'} + \cdots + e^{-n\Delta t/t_r'})$$

$$= S_1 \Sigma_n.$$

The total extension (E_n) at the end of the nth interval is related to the stress (s_n) for

$$E_n = nu_0 - u_n$$

and

$$u_0 = aS_1/k,$$

also

$$u_n = as_n/k.$$

Therefore

$$E_n = a(nS_1 - s_n)/k. \qquad (2)$$

This is an equation connecting elongation and unit stress at the nth reading and characterizes only the method of experimentation. It does not contain any explicit constant of the material except the geometric constant (a). Some information of qualitative value can be obtained by setting up the expression for the slope of the stress-strain curve. This cannot be done by forming the first derivative because (E_n) is not a continuous function of stress (s_n). However, the slope of the line joining any two adjacent points is a sufficiently close approximation and can easily be determined. By analogy with Eq. (2) the value of (E_{n-1}) can be written. The elongation increment (ΔE) is then formed by subtracting (E_{n-1}) from (E_n). The corresponding stress increment is (Δs). It follows then that

$$\Delta E = a(S_1 - \Delta s)/k.$$

But (s_n) is related to S_1 in such a manner that

$$\Delta s = S_1 e^{-n\Delta t/t_r'}.$$

The initial stress (S_1) can therefore be eliminated and the slope (g) can be set up as the ratio of (Δs) to (ΔE) and we have

$$g = k/a(e^{n\Delta t/t_r'} - 1).$$

The only quantity of intrinsic physical significance, namely (t_r'), has been introduced here by the elimination of (S_1). The slope (g) is a maximum when (n) is a minimum. The stress-strain curve should start from the origin with its maximum slope which then falls continuously as the number of the observation increases. For a given value of $(n\Delta t)$ the slope increases as the relaxation time (t_r') of the system as a whole increases. The slower the rate of stress relaxation the greater the slope of the stress-strain curve.

Assuming that the small initial slope of the wool curve (Fig. 7) is entirely due to the removal of kinks, we can say that the protein fibers, silk and wool, are well characterized by the above slope equation. Under the experimental conditions specified, they are predominantly plastic bodies in which Maxwell's idea of relaxation of stress by viscous yield is the main phenomenon. In the cellulosic fibers an additional elastic structure must be assumed for the purely viscous mechanism cannot give linear stress-strain relations. At the breaks A, B and C in the silk and nitrocellulose charts the value of the initial stress (S_1) was increased. On the assumption that the material exhibits viscous relaxation of stress it can be shown that the fractional change in slope is related, in sign and magnitude, to the change in (S_1) multiplied by a function of $e^{-n\Delta t/t_r'}$. To push the mathematical discussion farther will be of little value until a greater amount of experimental data is collected. Whether a fiber behaves as an elastic or viscous mechanism is largely a function of conditions such as moisture content and temperature. Much experimental information is necessary before a clear cut decision can be made between behavior which is an intrinsic property of the material or is merely a function of external conditions or

manipulation. Scott-Blair and Schofield[13, 14] have considered the significance of relaxation constants in soft materials and its bearing on Maxwell's ideas. Recent x-ray investigations[11, 15, 16, 17, 18, 19, 20] have shed much light on the underlying causes of the difference between textile fibers when under tension.

There is a fundamental molecular difference between the cellulosic fibers and wool. In the former the micelles are of great intrinsic strength. In ramie (i.e., pure cellulose) the micelles which are monoclinic crystals are oriented with their long axes parallel to the fiber axis and spirally about the fiber axis in the case of cotton. Tension is thus supported by the strong axial interatomic forces of the principal valence chains. There is little tendency for the micelles to rotate under tension. A linear stress-strain curve is to be expected. In rayon the micelles are not perfectly oriented. After a certain stress is exceeded the fiber yields plastically with turning of the micelles more nearly parallel to the fiber axis.[11]

It has been suggested by Astbury and his co-workers[17] that wool possesses elastic properties of a type entirely different from that of cellulose. Wool can be stretched 100 percent or more in the presence of steam or moisture and after a time recovers its initial length or even shrinks on release of tension. It exhibits two molecular forms of the basic constituent keratin—α-keratin in the unstretched state β-keratin when stretched. The α-keratin molecule extends under stress with an opening out of the separate molecular links to form the long zigzag polypeptide chain molecule of β-keratin. Two links of the α-keratin (identity period 5.15A) are stretched out into a chain six times as long.

In the case of cellulose fibers, ramie and cotton, it would be expected that before yield by micelle slip the principal valence chains supporting the tension will extend with a linear stress-strain relation. On the other hand, in wool there is considerable frictional resistance to extension because each link, in opening out, is impeded by its lateral neighbors. To get the full extension of wool, it is necessary to reduce the lateral interference by the use of moisture or steam. The characteristic difference between the stress-strain curves for the cellulosic fibers and wool, and probably silk, is therefore related to a structure finer than the micelle, i.e., to the molecule. Plastic yield in the protein fibers takes place by "molecular flow" in the cellulosic fibers by "micelle flow."

This paper represents part of the work done under a fellowship grant from the Textile Foundation. The writer wishes to express his appreciation of the hospitable extension of the facilities of Jefferson Laboratory by Director Lyman and the willingness of Professor Bridgman to act as director of the work. The assistance of Professor E. R. Schwarz of Massachusetts Institute of Technology in getting the writer properly started in an unfamiliar field is also greatly appreciated.

[13] G. W. Scott-Blair and R. K. Schofield, Proc. Roy. Soc. **A138**, 707 (1932).

[14] G. W. Scott-Blair, Physics **4**, 113 (1933).

[15] K. H. Meyer and H. Mark, *Der Aufbau der Hochpolymeren Organischen Naturstoffe*, Leipzig, 1930.

[16] K. R. Andress, Zeits. f. physik. Chemie **122**, 26 (1926); **136**, 379 (1928); **B2**, 380 (1929); **B4**, 190 (1929).

[17] W. T. Astbury and co-workers, J. Text. Sci. **4**, 1–5 (1931); J. Soc. Chem. Ind. **49**, 441 (1930); Nature **126**, 913 (1930); **127**, 663 (1931); Roy. Soc., Phil. Trans. **230**, 75–101 (1931); J. Text. Inst. **23**, 17–34 (1932).

[18] J. B. Speakman, J. Text. Inst. **15**, 529 (1924); **18**, 431 (1927); Trans. Faraday Soc. **26**, 61–69 (1930); Nature **128**, 1073; Proc. Roy. Soc. **A132**, 167–191 (1931).

[19] *Textile Research*—U. S. Institute for Textile Research Inc., M. I. T. Technology Press, 1932.

[20] Wayne A. Sisson, *X-ray Analysis of Fibers: Literature Survey*, Textile Research, Vol. III, March and April, 1933.

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A. B. Smith, Phys. Rev. **41**, 852 (1932).

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